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REISSUE PATENT APPLICATION
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Transmitted herewith for filing under 37 CFR §1.53(b) is the patent application for broadening reissue of U.S. Patent 5,571,571, issued November 5, 1996.

Inventor(s)/Applicant Identifier: MUSAKA et al.

For: METHOD OF FORMING A THIN FILM FOR A SEMICONDUCTOR DEVICE

- ☒ 9 sheet(s) of formal drawings; 22 pages of specification including description, claims and abstract; ☒ title page.
☒ Broadening Reissue Oath/Declaration Under 37 CFR §1.175 (PTO/SB/51 or 52).
☒ Foreign Priority Claim (35 U.S.C. 119)
☒ Priority Claim under 35 U.S.C §120
☒ Assent of Assignee and Offer to Surrender Patent.
☒ Certified Copy of Abstract of Title to U.S. Pat. #5,571,571.
☒ Two Return Receipt Postcards.

Claims 11-34 have been added to correct an error in the issued patent by reason of the patentees claiming less than they had a right to claim in the patent. Amendments have also been made to the specification to correct minor formal errors and omissions.

(Col. 1)

(Col. 2)

OTHER THAN
SMALL ENTITY

| FOR: | Claims in Patent | Number Filed in Reissue application | NO. EXTRA |
|--|------------------|-------------------------------------|-----------|
| BASIC FEE | | | |
| TOTAL CLAIMS (37 CFR 1.16(j)) | 10 | 31 | = 21 |
| INDEP CLAIMS (37 CFR 1.16(i)) | 2 | 6 | = 4 |
| [X] MULTIPLE DEPENDENT CLAIM PRESENTED | | | |

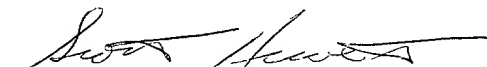
| RATE | FEE |
|-----------------|-----------|
| | \$790.00 |
| x \$22.00 = | \$462.00 |
| x \$82.00 = | \$328.00 |
| + \$270.00 = | \$ |
| TOTAL | \$1580.00 |

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Respectfully submitted,



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PATENT APPLICATION

**METHOD OF FORMING A THIN FILM FOR A SEMICONDUCTOR
DEVICE**

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METHOD OF FORMING A THIN FILM FOR A SEMICONDUCTOR DEVICE

This application is a reissue application of U.S. Patent No. 5,571,571,
which issued from application Ser. No. 08/259,584, which was a continuation-in-part
of application Ser No. 08/184,331 filed Jan. 19, 1994, now [abandon] abandoned,
entitled "A METHOD OF FORMING A THING FILM FOR A SEMICONDUCTOR
DEVICE".

The present invention relates to a method of forming a thin film for a
semiconductor device. More particularly, this invention relates to a plasma-enhanced
chemical vapor deposition (hereinafter PECVD) method for forming a silicon oxide
thin film on a semiconductor substrate.

BACKGROUND OF THE INVENTION

PECVD provides a well known method of depositing a thin film. A
body is placed in a vacuum reaction chamber and a reaction gas is introduced into the
chamber. The gas is activated by means of a plasma discharge created in the chamber.
This causes the reaction gas to react and deposit a thin film of a material on the
surface of the body.

The methods of creating a plasma in the reaction chamber for PECVD
include the method in which an electric power source having a frequency of 13.56
MHz or other frequency is applied to a pair of opposed electrodes within the reaction
chamber. The deposition rate and the quality of the deposited thin film can be
controlled by adjusting the power of this electric power source. Another method of
creating a plasma in a reaction chamber uses a microwave radiation of 1.54 GHz,
introduced into the reaction chamber by means of a wave guide. This method is
known as ECR plasma CVD. Gases used to deposit a thin film of silicon oxide on a

semiconductor substrate include alkoxy silicates such as tetraethylorthosilicate, $(C_2H_5O)_4-Si$, (hereinafter TEOS) and silane, SiH_4 .

With the recent development of high density semiconductor integrated circuit devices (VLSI devices) there has been created an urgent need for techniques that can create ultrafine configurations in the submicron range. In order to respond to this demand, the possibility of using conventional techniques to create submicron configurations was considered by conducting an empirical study on the configuration of thin films produced by conventional plasma-enhanced CVD methods.

Each of FIGS. 1A to 1F, 2A to 2F and 4A to 4F are cross sectional views of tracings made of the outlines shown in microphotographs of the longitudinal configurations of actual devices, with the height and width of the devices being indicated by the unit scale in the figures.

Referring to FIGS. 1A to 1F, there are shown sectional views of semiconductor devices 10a to 10f, each comprising a substrate 12a to 12f having a layer 14a to 14f of an insulating material, such as silicon oxide, on a surface 16a to 16f thereof. A plurality of spaced, parallel lines 18a to 18f of a conductive material, such as aluminum, are on the insulating layers 14a to 14f, and are in turn coated with a layer 20a to 20f of an insulating material, such as silicon oxide. The conductive strips 18a to 18f have different widths, strip 18a being the widest and strip 18f being the narrowest. In addition, the spacing between the conductive strips 18a to 18f varies as well, the strips 18a being spaced apart the greatest distance and the strips 18f being spaced apart the closest distance. The insulating coatings 20a to 20f were formed by conventional PECVD wherein a reaction gas of silane (50 sccm) and oxygen at a flow rate one-tenth that of silane was passed into a reaction chamber held at a pressure of 3 Torr. A single 13.56 MHz frequency electric power source between a pair of opposing electrodes spaced 180 mils apart in the chamber was used to form a plasma between the electrodes.

As can be seen in FIGS. 1A to 1F, the sidewalls of the spaces in the silicon oxide coatings 20a to 20f have rounded edges and are thicker over the aluminum strips 18a to 18f than between the aluminum strips 18a to 18f. Thus variously shaped gaps are formed in the silicon oxide coatings 20a to 20f. As the

width of the aluminum strips 18a to 18f become narrower, and the spacing between the aluminum strips 18a to 18f also become narrower, irregularly shaped sidewalls are formed and the gaps in the silicon oxide coating 20a to 20f vary in width. In particular, the gaps are narrower at the center of the sidewalls than at the bottom of the sidewalls. This leads to the formation of voids in the coatings 20 as the gaps are filled in. It is believed that because silane is very reactive, the oxidation reaction occurs in the gaseous phase, producing the non-uniform, poor deposition profiles seen in FIGS. 1A to 1F. Thus the use of silane as the reaction gas for deposition of silicon oxide films over conductive metal lines has severe limitations as devices on a semiconductor substrate become smaller and more devices are produced on a single substrate.

FIGS. 2A to 2F illustrate a cross sectional view of semiconductor devices 22a to 22f, similar to those of the semiconductor devices 10a to 10f of FIGS. 1A to 1F. The semiconductor devices 22a to 22f comprise a substrate 24a to 24f of a semiconductor material, such as silicon, having a layer 26a to 26f of an insulating material thereon, such as silicon oxide, on a surface 28a to 28f thereof. A plurality of spaced parallel strips 30a to 30f of a conductive material, such as aluminum, are deposited on the insulating layers 26a to 26f. The conductive strips 30a to 30f are in turn coated with a layer 32a to 32f of an insulating material such as silicon oxide. The conductive strips 30a to 30f have different widths, the conductive strip 30a being the widest, and 30f being the narrowest. Also the spacing between the conductive strips 30a to 30f varies, the spacing between the conductive strips 30a being the widest and the spacing between the conductive strips 30f being the narrowest.

In FIGS. 2A to 2F, the insulating layers 32a to 32f were formed by PECVD using TEOS as the reactive gas, and a single 13.56 MHz power source. As can be seen from FIGS. 2A to 2F, the sidewalls of the silicon oxide deposit are less rounded than those shown in Figs. 1A-1F, although the gaps between the openings in the silicon oxide layers 32a to 32f narrow as the conductive strips 30a to 30f become narrower and the spacing between them becomes narrower. Thus the use of TEOS to form silicon oxide films has advantages over the use of silane for small features. However, these films finally also form voids, particularly when the spacing between

the strips 30a to 30f is less than 0.5 micron, see layers 32d to 32f. Thus although the deposition profile is much more uniform than the profiles of FIGS. 1A to 1F using silane as the precursor gas, as the aluminum lines become narrower and closer together, voids are formed in the growing film. Thus the use of TEOS to grow silicon oxide films over stepped topography is also limited, and is inadequate for submicron lines and spaces as shown particularly in FIGS. 2D to 2F.

Thus it would be desirable to be able to deposit silicon oxide films over conductive lines that are spaced closer than 0.5 micron, but that do not form voids in the layer. Further, it is desired to improve the quality of the silicon oxide films.

Other prior art workers have addressed this problem. Foster et al., U.S. Pat. No. 4,667,365 and assigned to the same assignee as the present invention, discloses adding CF_4 or NF_3 to silane while depositing silicon oxide, and to creating the plasma using either a single power source or more than one power source having different frequencies, and using magnetron enhanced processing. Foster et al. explain that the fluorine-containing gases produce etching during deposition, thereby controlling the sidewall profiles and improving the conformality of the depositing film and reducing the formation of voids. However, the deposition rate was adversely affected by the addition of the fluorine-containing gases.

Another process that has been used to improve the ability of the SiO_2 film to adequately fill the gaps between closely spaced apart metal lines comprises an atmospheric pressure (i.e., 760 Torr) CVD method in which TEOS gas is utilized with a source of oxygen gas comprising a mixture of O_2 and O_3 gases, i.e., an ozone-TEOS precursor gas mixture. This method however, leads to the formation of a silicon oxide film having a high hygroscopicity, which can lead to degradation in the moisture resistance of the final integrated circuit structure, which is not tolerable.

Weise et al. PCT application US92/04103, describes the reaction on an inorganic substrate of unsubstituted silane (SiH_4) together with a halogen-containing gas and an oxygen-containing gas by PECVD or ECR CVD techniques.

Alternatively the precursor gas can be an organosilane. An etchant is added along with the precursor gas or gases. Suitable etchants listed include fluorine-containing

compounds and halogens, but the preferred etchants are HF or NF_3 . Sulfur-based or carbon-based etchants are not preferred however, because it is stated that residual sulfur or carbon remains in the films, which is undesirable. Halogens are not preferred either, because they corrode the reaction chamber and other equipment. As is well known, NF_3 and HF are also corrosive, particularly to quartz parts. The addition of NF_3 to the silicon oxide film reduces intrinsic stress in the film, and also reduces the amount of hydrogen present in the film, which has a high dielectric constant. However, this process leads to films having low compressive stress, which leads to semiconductor devices with unsatisfactory electrical properties, and inferior mechanical properties. The process also exhibits low deposition rates.

Thus a method of depositing silicon oxide films on semiconductor substrates, and particularly over submicron conductive metal lines, that is conformal even over submicron lines and spaces, and that is of high quality, but without sacrificing deposition rate unduly, would be highly desirable.

SUMMARY OF THE INVENTION

The present invention is directed to a method of depositing conformal silicon oxide films at high deposition rates that can fill the spaces between closely spaced conductive metal lines without the formation of voids, which films are of high quality. A plasma precursor gas mixture of TEOS and a selected fluorine-containing gas is introduced into a vacuum chamber containing a substrate to be coated that is connected to a source of power. When the power is turned on, a plasma is formed and high quality silicon oxide films deposit on the substrate. The power source may be of a single frequency or multiple power sources having different frequencies can be employed. Different fluorine-containing gas can be employed depending on the apparatus used to deposit the silicon oxide films.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1A, 1B, 1C, 1D, 1E and 1F are cross-sectional views of semiconductor devices formed by a prior art PECVD method with the devices having

conductive strips of various widths and various spacings using silane as a plasma precursor gas source of silicon.

FIGS. 2A, 2B, 2C, 2D, 2E and 2F are cross-sectional views of semiconductor devices formed by another prior art PECVD method with the devices having conductive strips of various widths and various spacings using TEOS alone as a plasma precursor gas source of silicon.

FIG. 3 is a schematic sectional view of one form of a deposition apparatus having multiple power sources which can be used to carry out the method of the present invention.

FIGS. 4A, 4B, 4C, 4D, 4E and 4F are cross-sectional views of semiconductor devices formed by PECVD using a power source having multiple frequencies with the devices having conductive strips of various widths and various spacings in accordance with the present invention.

FIG. 5 is a schematic sectional view of another form of a deposition apparatus having multiple power sources which can be used to carry out the method of the present invention.

FIG. 6 is a schematic sectional view of a deposition apparatus having a single power source which can be used to carry out the **[method]** method of the present invention.

FIGS. 7A, 7B, 7C, 7D, 7E and 7F are cross-sectional views of semiconductor devices formed by PECVD using a power source of a single frequency with the devices having conductive strips of various widths and various spacings in accordance with the present invention.

FIG. 8A is an X-ray photoelectron spectrum (XPS) graph of a silicon oxide layer deposited in accordance with the present invention.

FIG. 8B is a graph of 1s binding energy for fluorine showing inorganic fluorine bonds.

FIG. 9 is a graph of fluorine concentration in a silicon oxide film of the invention versus the Si/F reactant ratio.

FIG. 10 is a graph of fluorine concentration in atomic percent of silicon oxide films of the invention versus C_2F_6 gas flow using TEOS as the reactant gas.

FIG. 11 is a graph of fluorine concentration in atomic percent of silicon oxide films of the invention versus dielectric constant.

FIG. 12 is a graph of wet etch rate versus C_2F_6 gas flow using TEOS as the reactant gas for silicon oxide films of the invention.

FIG. 13 is a graph of stress versus C_2F_6 gas flow using TEOS as the reactant gas for silicon oxide films of the invention.

DETAILED DESCRIPTION OF THE INVENTION

In one embodiment of the present invention, a plasma is created within a reaction chamber by means of two electrical power sources having different frequencies. A high frequency of about 13.56 MHz and a low frequency of between about 50 KHz and about 1000 KHz, preferably about 400 KHz, are used. A reaction gas comprising a mixture of TEOS and a halogen gas selected from a fluorine, a chlorine or a bromine gas, is introduced into the reaction chamber and subjected to the plasma. The ratio of the TEOS to halogen can vary. Increasing the amount of halogen gas decreases the deposition rate, which can be from about 4800 to about 6000 angstroms per minute. Thus a ratio of about 1:1 for TEOS to halogen is preferred for this embodiment. Suitable fluorine-containing gases include CF_4 , C_2F_6 , NF_3 , CHF_3 , CH_2F_2 , F_2 , SF_6 and the like. Suitable chlorine-containing gases include CCl_4 , Cl_2 , HCl and the like. Suitable bromine-containing gases include HBr and the like.

The thin film deposited by the above method when deposited over conductive strips has been found to have a smooth, tapering configuration, with no voids even at very small widths of the conductive strips and at submicron spacings. Also, since the sidewalls of the deposited layer have superior fineness, the above method is superior in terms of the control it affords over film quality. In addition, when the film is formed using a fluorine-containing gas, the deposited layer also

includes fluorine. This fluorine in an insulating film of silicon dioxide lowers the dielectric constant of the film, which in turn enhances the electrical properties of any transistors formed using the method of the present invention. The silicon oxide films of the invention are stable in the presence of moisture.

5 Referring now to FIG. 3, there is shown one type of a deposition apparatus 34 which can be used to carry out the method of the present invention. The deposition apparatus 34 comprises an insulated deposition vessel 36 having an airtight reaction chamber 38. A pair of electrodes 40 and 42 are in spaced, substantially parallel relation within the reaction chamber 38. The electrode 40 serves as a support
10 for a body 44, such as a semiconductor substrate, on which a coating is to be deposited, and is connected to ground potential. The electrode 42 has an inlet tube 46 extending therefrom and out of the vessel 36 through which a reaction gas can be admitted into the reaction chamber 38. An outlet tube 48 extends from a wall of the reaction vessel 36 to permit gases to be exhausted from the reaction chamber 38. A
15 heater 50 is provided along the electrode 40 to control the temperature of the body 44 during deposition.

The electrode 42 is connected to a first power source 52 for providing a high frequency, typically about 13.56 MHz, oscillation to the electrode 42. An impedance matching circuit 54 is provided between the high frequency power source
20 52 and the electrode 42. The electrode 42 is also connected to a second power source 56 for providing a lower frequency, typically about 400 KHz, oscillation to the electrode 42. Between the low frequency power source 56 and the electrode 42 are an impedance matching circuit 58 and a high frequency cut-off filter circuit 60 for blocking the passage of any high frequency components. By simultaneously applying
25 to the electrode 42 electrical power of two different frequencies, i.e., high and low frequencies, a plasma is created within the reaction chamber 38.

To deposit a layer of a material, such as silicon dioxide, on the surface of a body 44, such as a semiconductor substrate, in the apparatus 34 using the method of the present invention, the body 44 is placed in the chamber 38 and on the electrode
30 40. A reaction gas of a mixture of a fluorine gas, such as NF_3 , and TEOS gas is introduced into the chamber 38 through the inlet tube 46. The power sources 52 and

56 are turned on to simultaneously provide a high frequency power and a lower frequency power to the electrodes 40 and 42. The ratio between the power outputs from the high frequency source 52 and the lower frequency source 56 is suitably adjusted to form a plasma within the chamber 38 and between the electrodes 40 and 42. The reaction gas is subjected to the plasma, causing the reaction gas to react and deposit a thin film of silicon oxide on the exposed surface of the body 44.

Referring to FIGS. 4A to 4F, there are shown sectional views of semiconductor devices 62a to 62f formed by the method of the present invention in an apparatus 34 described above. Each of the semiconductor devices 62a to 62f comprises a semiconductor substrate 64a to 64f, typically of silicon, having on a surface 66a to 66f thereof a layer 68a to 68f of silicon dioxide. On the silicon dioxide layer 68a to 68f are a plurality of spaced, substantially parallel strips 70a to 70f of aluminum. The aluminum strips 70a to 70f are similar to the conductive wiring of an integrated circuit. A layer 72a to 72f of silicon dioxide is coated over the aluminum strips 70a to 70f and the surface of the silicon dioxide layers 68a to 68f between the aluminum strips 70a to 70f. The aluminum strips 70a to 70f vary in width and spacing, with the aluminum strips 70a in FIG. 4A being the widest and having the widest spacing therebetween, and the aluminum steps 70f in FIG. 4F being the narrowest and being the most closely spaced.

The silicon dioxide layers 72a to 72f were deposited over the aluminum strips 70a to 70f by the above described method. For this method, the pressure in the reaction chamber 38 was 5 Torr, and the spacing between the electrodes 40 and 42 was 250 mils. A flow of TEOS and a helium carrier gas at 480 sccm was provided in the reaction chamber 38. A flow of C_2F_6 at 400 sccm and a flow of oxygen at 700 sccm was also provided in the reaction chamber 38. A high frequency of 13.56 MHz at a power of 80 watts was applied to the electrode 42, and a low frequency of 400 KHz at a power of 90 watts was also applied to the electrode 42.

When the widths of the respective aluminum strips and of the corresponding spaces between the strips are comparatively large, as shown in FIGS. 4A to 4D, the sidewalls of the silicon dioxide layers 72a to 72d have a smoothly

tapered configuration. However, even when the widths of the respective aluminum strips and of the corresponding spaces between the strips is in the submicron range, as shown in FIG. 4E, the sidewall configuration of the silicon dioxide layer 72e is straight, and the possible creation of voids is greatly reduced. When the width of the respective aluminum strips and the corresponding spaces therebetween is reduced even further, in the submicron range, as shown in FIG. 4F, the spaces between the aluminum strips 70f are buried by the silicon oxide layer 78f, without the formation of any voids in the film. Since the sidewalls obtained with the configurations shown in FIGS. 4E and 4F have a fine compositional structure, an enhancement of the quality is achieved. The compressive stress of the above film was found to be 1×10^9 dynes/cm².

Although applicants are not to be bound by any theory, it is believed that the reason that voids are reduced and that the walls of the silicon oxide thin films deposited by the above-described method have a tapered configuration is that at the same time that the deposit is formed on the upper surface of the aluminum strips, the deposited thin film is subjected to etching by the halogen-containing gas that smooths the sidewalls. In addition, when the deposited silicon oxide film includes fluorine, the dielectric constant of the silicon oxide is lowered. Thus, in cases such as those wherein the aluminum strips are used as wiring between gates of MOSFETs for the purpose of connecting the gate electrodes of MOSFETs, it is possible to realize a MOSFET with good electrical characteristics.

Referring to FIG. 5, there is shown another apparatus 74 which can be used to carry out the method of the present invention. Apparatus 74 is an ECR plasma CVD device and comprises a reaction vessel 76 having a deposition chamber 78 and a plasma creation chamber 80 over and opening into the deposition chamber 78. An electrode 82 is within the deposition chamber 78 and is adapted to support a body 84, such as a semiconductor substrate to be coated. A microwave wave guide tube 86 extends to the top of the plasma creation chamber 80 and is mounted on a window 88 over an opening in the plasma creation chamber 80. The wave guide tube 86 is adapted to deliver microwave power, typically about 2.45 GHz, to the plasma

creation chamber 80. The electrode 82 is connected to a high frequency, typically about 13.56 MHz, power source 90.

A cooling chamber 92 surrounds the plasma creation chamber 80. Inlet and outlet pipes 94 and 96 respectively extend into and away from the cooling chamber 92 and are adapted to provide a flow of a cooling fluid through the cooling chamber 92. A gas inlet tube 98 extends into the plasma creation chamber 80 and is adapted to deliver a plasma forming gas into the plasma creation chamber 80. A gas inlet tube 102 extends into the deposition chamber 78 and a gas exhaust opening 83 is also in the deposition chamber 78.

To carry out the method of the present invention in the apparatus 74, a body 84 to be coated is placed on the electrode 82. The microwave power is fed into the plasma forming chamber 80 simultaneously with the high frequency power being applied to the electrode 82. A plasma forming gas is fed into the plasma forming chamber 80 where a plasma is formed by the application of the two powers of different frequencies. The plasma is drawn from the plasma forming chamber 80 into the deposition chamber 78. The reaction gas, a mixture of TEOS and a halogen-containing gas, is fed into the vessel 76 where it is reacted by the plasma to form silicon oxide which deposits on the surface of the body 84.

In addition, the present method can also be carried out using only a single frequency power source for forming a plasma between the electrodes, as shown in FIG. 6.

The apparatus of FIG. 6 is similar to the apparatus of FIG. 3, except that only a single power source is employed. Referring to the deposition apparatus 200 of FIG. 6, an airtight reaction chamber 201 includes a pair of electrodes 203 and 204 spaced apart and substantially parallel to each other. The electrode 204 serves as a support for a body 205 to be coated. The electrode 203 has an inlet tube 206 extending from the reaction chamber 201 for the introduction of reaction gases. An exhaust port 202 also extends from a wall of the chamber 201 to permit gases to be exhausted from the chamber 201. A heater 207 is provided along the electrode 204 to control the temperature of the body 205 during deposition.

The electrode 203 is connected to a power source 208 for providing a high frequency, typically 13.56 MHz, oscillation to the electrode 203. An impedance matching circuit 209 is provided between the high frequency power source 208 and the electrode 203.

5 A silicon oxide film was deposited in accordance with the present invention using the apparatus of FIG. 6, maintaining a pressure of 5 Torr in the chamber, a spacing between the electrodes of 250 mils, a flow of vaporized TEOS (480 sccm) adding oxygen gas at a ratio of TEOS:O₂ of 1:10, and C₂F₆ as the halogen additive gas at a flow rate such that the volume ratio of O₂:C₂F₆ is 3:1. TEOS was
10 vaporized by passing a carrier gas, such as helium, through a heated liquid TEOS [resevoir] reservoir. A carrier gas flow of 400 sccm of helium passed into the [resevoir] reservoir will pick up about 80 sccm of TEOS. Thus a 480 sccm gas flow will be measured for the TEOS flowing into the reaction chamber. Thus about 5 parts by volume of carrier has per volume of TEOS vapor will flow into the reaction
15 chamber.

Referring to FIGS. 7A to 7F, there are shown sectional views of semiconductor devices 300a to 300f comprising a semiconductor substrate 302a to 302f, typically of silicon, having on a surface 304a to 304f thereof a layer 306a to 306f of silicon oxide. On the silicon oxide layers 306a to 306f are a plurality of
20 spaced, substantially parallel strips 308a to 308f of aluminum. The aluminum strips 308a to 308f are similar to [conductirve] conductive wiring for an integrated circuit. A layer 310a to 310f of silicon oxide deposited in accordance with the invention is coated over the aluminum strips 308a to 308f and the surface of the silicon oxide layers 310a to 310f between the aluminum strips 308a to 308f. The aluminum strips
25 308a to 308f vary in width and spacing as in FIGS. 4A to 4F.

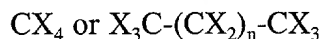
The silicon oxide layers 310a to 310f were deposited over the aluminum strips 308a to 308f in the reaction chamber of FIG. 6 in similar fashion, i.e., same gases and gas flows and reaction conditions, to the films deposited as shown in FIGS. 4A to 4F, except that only a single power source having a frequency
30 of 13.56 MHz was employed.

It is apparent that no voids were formed in the silicon oxide films 310a to 310f.

The silicon oxide film obtained contained about 4.3% of fluorine. In this case, using a single frequency, the deposition rate of the silicon oxide was reduced to about 2500-3000 angstroms per minute. The compressive stress of this film was about 2×10^8 dynes/cm².

FIG. 8A is a graph of an XPS of the above film. The binding energy is depicted for oxygen, fluorine and silicon. The fluorine 1s level at about 687 show that the fluorine is bonded to an inorganic element, such as Si-F, rather than an organic bond such as C-F-C. FIG. 8B is a graph of 1s binding energy for fluorine, as set forth in "Handbook of X-ray Photoelectron Spectroscopy" of Perkin-Elmer Company. This shows two points, "A" and "B". "A" is the binding energy of fluorine obtained for the silicon oxide film made by the above process at a concentration of 4.3 atomic percent of fluorine; and "B" is the binding energy of fluorine obtained for a silicon oxide film made by the above process at a concentration of 7.3 atomic percent of fluorine. These points are both below the kinetic energy line 651, as is a known Si-F compound, CoSiF. The 1s binding energy of fluorine for an organic or polymeric C-F bond is much higher- at the 654 line. Thus both samples "A" and "B" show the fluorine in the silicon oxide film is present as an inorganic bond, e.g., bonded to silicon, rather than an organic bond, e.g., bonded to carbon.

When the above method of preparing silicon oxide from TEOS was repeated except using NF₃ as the halogen source, poor deposition profiles were obtained. Thus when only a single frequency power source apparatus is employed, halocarbons having the formulas



wherein X is hydrogen or halogen, with the proviso that at least one halogen is present, and n is an integer of 0 to 5, are employed. However, fluorocarbons, such as C₂F₆ or CF₄ and the like, are the halogens of choice.

As the fluorine content of the silicon oxide film deposited in accordance with the invention increases, the dielectric constant of the films is

reduced, improving the electrical properties of the film. Higher fluorine-containing gas flow rates during deposition also improve the gap filling capability of the silicon oxide films and increase the wet etch rate, while reducing the deposition rate and refractive index (R.I.).

5 The application of low frequency power decreases the deposition rate, but improves compressive stress, slightly increases the wet etch rate, lowers R.I. and increases the gap filling capability. The application of high frequency power slightly reduces the deposition rate, does not affect the compressive stress of the films, slightly increases the wet etch rate, slightly decreases the R.I. and slightly increases
10 the gap filling capability.

 Thus, in order to maximize the deposition rate, silicon oxide film quality, and obtain conformal, low dielectric constant silicon oxide films, it is preferred that the concentration of fluorine in the film be about 2.5 atomic percent or higher.

15 FIG. 9 is a graph of fluorine concentration in atomic percent versus Si/F reactant ratio of TEOS:F-containing gas. Thus if the desired atomic percentage of fluorine in the silicon oxide film is 2.5 atomic percent, the Si/F reactant ratio should be about 14:1.

20 FIG. 10 is a graph of fluorine concentration in atomic percent versus C_2F_6 gas flow. For a film containing 2.5 atomic percent of fluorine, the C_2F_6 gas flow rate should be about 125 sccm.

 FIG. 11 is a graph of dielectric constant versus fluorine concentration in the silicon oxide film. It can be seen that as fluorine concentration rises, dielectric constant is lowered.

25 FIG. 12 is a graph of the wet etch rate of a silicon oxide film versus C_2F_6 flow rates, illustrating that there is an increase in wet etch rate as fluorine concentration increases to a maximum level.

 FIG. 13 is a graph of C_2F_6 flow rate versus stress of the silicon oxide films, showing reduced stress with higher C_2F_6 flow rates and higher fluorine
30 concentration in the films.

We have found that an optimum ratio of silicon to fluorine of about 14:1 in the precursor gases is preferred in our process to minimize formation of voids over submicron lines and spaces, and to maximize the physical and electrical properties of the film, without unduly sacrificing deposition rates. The resultant film contains about 2.5 atomic percent of fluorine.

Although the present invention has been described in terms of specific embodiments, the invention is only meant to be limited by the scope of the appended claims. Various changes in the processing parameters, plasma precursor gases and equipment can be made as will be well known to one skilled in the art.

We Claim:

1 1. A method of forming a conformal thin film of silicon oxide on a
2 substrate having spaced conductive lines thereon comprising the steps of:
3 mounting a substrate onto a substrate support in a vacuum chamber;
4 forming a plasma in the vacuum chamber in a region above the
5 substrate by means of an electrical power source from a reaction gas comprising a
6 mixture of tetraethylorthosilicate and a fluorine-containing halocarbon gas selected
7 from the group consisting of CX_4 and $CX_3-(CX_2)_n-CX_3$ wherein X is hydrogen or
8 halogen and n is an integer from 0 to 5 with the proviso that at least one X is
9 fluorine; and
10 subjecting the substrate to the plasma so as to deposit a layer of silicon
11 oxide containing at least about 2.5 atomic percent of fluorine onto the substrate
12 without the formation of voids in the film.

1 2. The method of claim 1 wherein the plasma is created from the
2 tetraethylorthosilicate and C_2F_6 .

1 3. The method of claim 1 wherein the plasma is created by means
2 of two power sources having different frequencies.

1 4. The method of claim 3 wherein the plasma is created by means
2 of one power source having a frequency of about 13.56 MHz and a second power
3 source having a frequency of between 50 KHz and 1000 KHz.

1 5. The method of claim 4 wherein the second power source has a
2 frequency of about 400 KHz.

1 6. The method of claim 1 wherein a single power source having a
2 frequency of about 13.56 MHz is used.

1 7. The method of claim 1 wherein said power source is a source of
2 microwave power.

1 8. A method of forming a conformal thin film of silicon oxide
2 over a substrate having spaced conductive lines thereon in a plasma chamber
3 comprising
4 mounting a substrate in said chamber;
5 introducing into the chamber in a region above said substrate as a
6 plasma precursor gas vaporized tetraethylorthosilicate in a carrier gas including
7 oxygen and a fluorocarbon selected from the group consisting of
8 CX_4 and $CX_3-(CX_2)_n-CX_3$
9 wherein X is hydrogen or fluorine and n is an integer from 0 to 5 with
10 the proviso that at least one X is fluorine;
11 and thereafter forming a plasma therefrom, so as to deposit a layer of
12 silicon oxide containing at least about 2.5 atomic percent of fluorine over said
13 conductive lines.

1 9. A method according to claim 8 wherein the plasma precursor
2 gas contains a ratio of silicon:fluorine of about 14:1.

1 10. A method according to claim 8 wherein the conductive lines are
2 less than 1 micron in width and no more than 1 micron apart.

1 11. In a processing chamber, a method of depositing a layer having
2 a predetermined intrinsic stress level over a substrate, the method comprising:

3 (a) distributing a halogen source to said processing chamber at a
4 selected rate, said selected rate being chosen according to said predetermined stress
5 level;

6 (b) introducing a process gas comprising silicon, oxygen and said
7 halogen source into said chamber; and

8 (c) forming a plasma from said process gas to deposit said layer
9 having said predetermined intrinsic stress level over said substrate.

1 12. The method of claim 11 wherein said predetermined stress level
2 is a compressive stress level.

1 13. The method of claim 11 wherein said halogen source comprises
2 a fluorine source.

1 14. The method of claim 13 wherein said fluorine source is selected
2 from the group consisting of CF₄, C₂F₆, SiF₄, and TEFS.

1 15. The method of claim 14 wherein said silicon source comprises
2 TEOS.

1 16. The method of claim 15 wherein said predetermined intrinsic
2 stress level is between about -1.0x10⁹ dynes/cm² and -0.5x10⁹ dynes/cm².

1 17. The method of claim 16 wherein a dielectric constant of said
2 layer is between about 3.8 to 4.1.

1 18. The method of claim 13 further comprising steps of:

2 (d) repeatedly performing steps (a) through (c) to deposit a
3 halogen-doped silicon oxide film on a plurality of substrates;

4 (e) measuring the intrinsic stress of said deposited halogen-doped
5 silicon oxide film on each of said plurality of substrates; and

6 (f) if said intrinsic stress of said deposited halogen-doped silicon
7 oxide films is too high, increasing said selected rate at which said halogen source is
8 introduced during deposition of a halogen-doped silicon oxide film over a
9 subsequently processed substrate to lower the intrinsic stress of said subsequently
10 deposited halogen-doped silicon oxide film, and if said intrinsic stress of said

deposited halogen-doped silicon oxide films is too low, decreasing said selected rate at which said halogen source is introduced during deposition of a halogen-doped silicon oxide film over a subsequently processed substrate to increase the intrinsic stress of said subsequently deposited halogen-doped silicon oxide film.

19. The method of claim 13 wherein said selected rate is determined from a database of measured intrinsic stress levels of previously deposited films.

20. The method of claim 11 wherein said processing chamber comprises a high-density plasma chemical vapor deposition chamber and said plasma is formed by application of radio-frequency power to a coil.

21. In a processing chamber, a method of depositing a layer having a selectively varied stress level on a substrate, the method comprising:

(a) distributing a halogen source to said processing chamber at a first selected rate, said first selected rate being chosen according to a first predetermined stress level;

(b) introducing a process gas comprising silicon, oxygen and said halogen source into said chamber;

(c) forming a plasma from said process gas to deposit a first portion of the layer having said first predetermined intrinsic stress level over said substrate; and then

(d) distributing the halogen source to said processing chamber at a second selected rate, said second selected rate being chosen according to a second predetermined stress level to deposit a second portion of the layer on the first portion of the layer, said second portion of the layer having said second predetermined intrinsic stress level.

22. The method of claim 21 where said first predetermined stress level is compressive and said second predetermined stress level is tensile.

1 23. The method of claim 21 where said first predetermined stress
2 level is tensile and said second predetermined stress level is compressive.

1 24. A substrate processing system comprising:
2 a housing for forming a vacuum chamber;
3 a substrate holder, located within said housing, for holding a substrate;
4 a gas delivery system configured to introduce a process gas into said
5 vacuum chamber;
6 a plasma generation system configured to form a plasma from said
7 process gas;
8 a controller for controlling said gas delivery system and said plasma
9 generation system; and
10 a memory coupled to said controller comprising a computer readable
11 medium having a computer readable program embodied therein for directing
12 operation of said substrate processing system, said computer readable program
13 comprising:
14 a first set of instructions for controlling said gas delivery system to
15 introduce a process gas comprising silicon, oxygen, and a halogen source into said
16 gas mixing area; and
17 a second set of instructions for controlling said plasma generation
18 system to form a plasma from said gases by said first set of instructions to deposit a
19 layer over said substrate;
20 whereby said first set of instructions controls said gas delivery system
21 to introduce said halogen source into said gas mixing area at a selected rate so that
22 said deposited layer has a predetermined intrinsic stress level.

1 25. The substrate processing system of claim 24 wherein said first
2 set of instructions controls said gas delivery system to introduce a fluorine source as
3 said halogen source into said gas mixing area at a selected rate so that said deposited
4 layer has a stress level of between -1.0 to -0.5x10⁹ dynes/cm².

1 26. The substrate processing system of claim 24 wherein said first
2 set of instructions controls said gas delivery system to introduce said fluorine source
3 into said chamber at a rate that is about 20% or less of the total gas flow into said
4 chamber.

Accepted for filing

METHOD OF FORMING A THIN FILM FOR A SEMICONDUCTOR DEVICE

ABSTRACT OF THE DISCLOSURE

5 A method of forming conformal, high quality silicon oxide films that
can be deposited over closely spaced, submicron lines and spaces without the
formation of voids, comprises forming a plasma of TEOS and a selected halogen-
containing gas in certain ratios. By proper control of the energy sources that create
the plasma, the proper selection of the halogen-containing gas and selection of other
10 processing parameters, high deposition rates can also be achieved.

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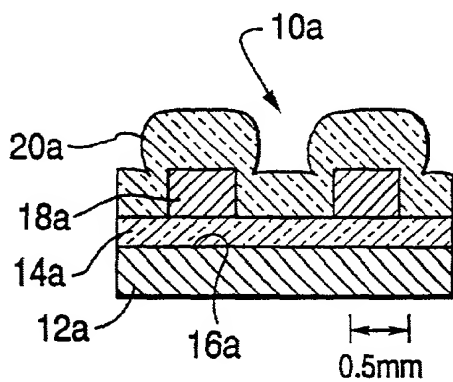


FIG. 1A
PRIOR ART

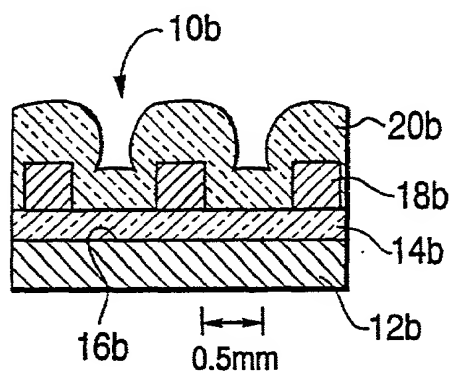


FIG. 1B
PRIOR ART

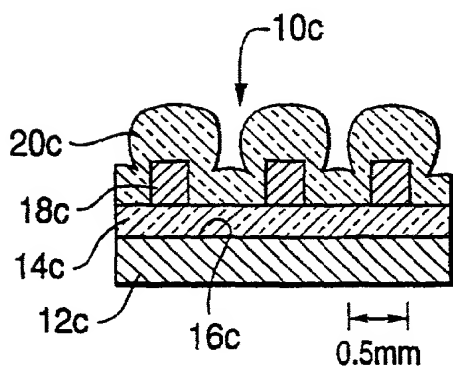


FIG. 1C
PRIOR ART

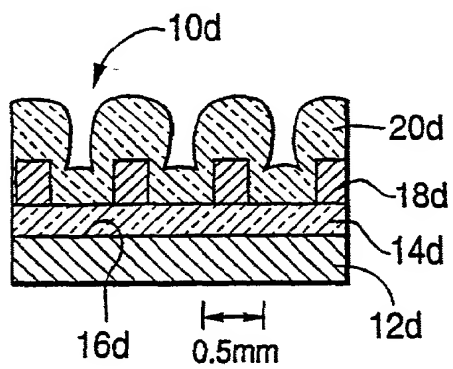


FIG. 1D
PRIOR ART

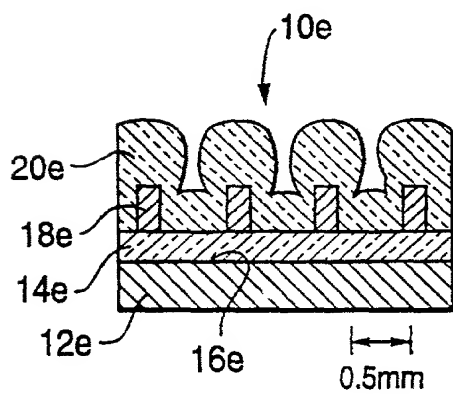


FIG. 1E
PRIOR ART

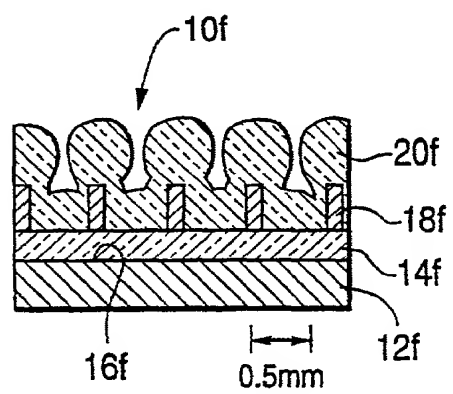


FIG. 1F
PRIOR ART

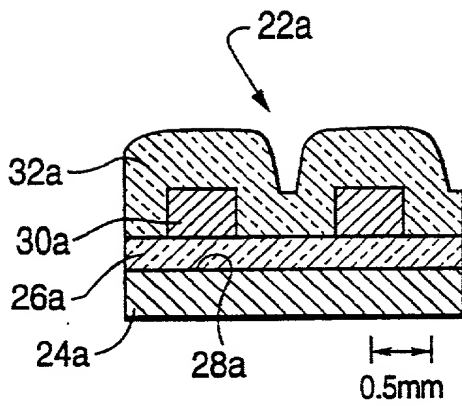


FIG. 2A
PRIOR ART

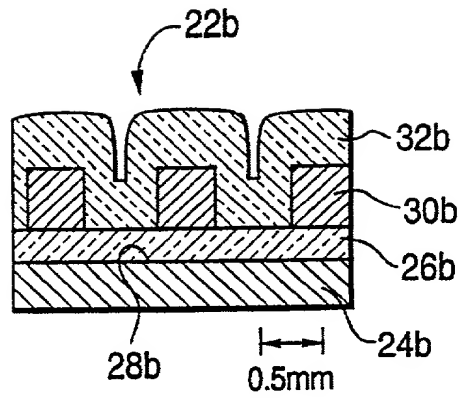


FIG. 2B
PRIOR ART

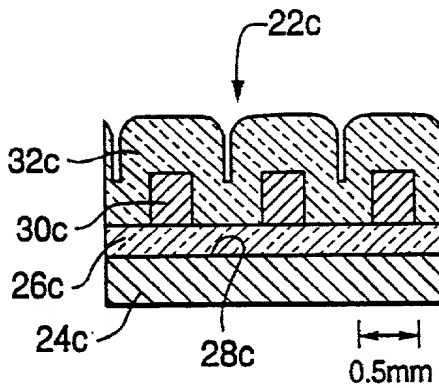


FIG. 2C
PRIOR ART

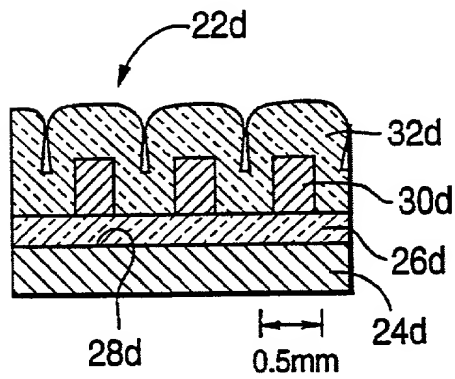


FIG. 2D
PRIOR ART

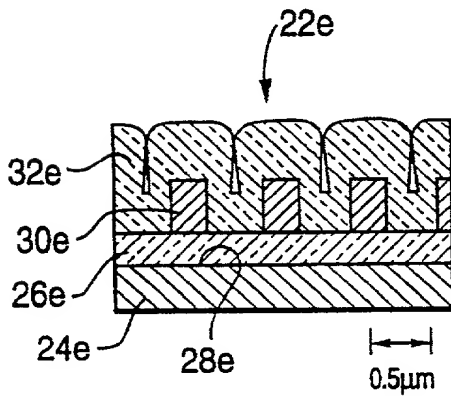


FIG. 2E
PRIOR ART

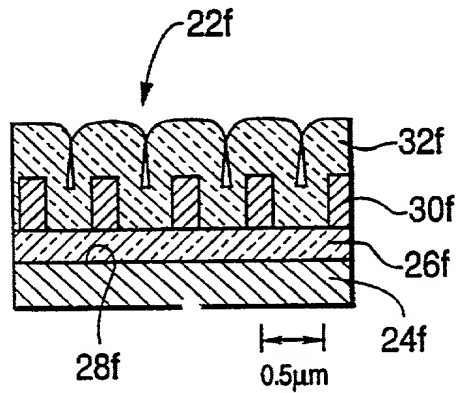
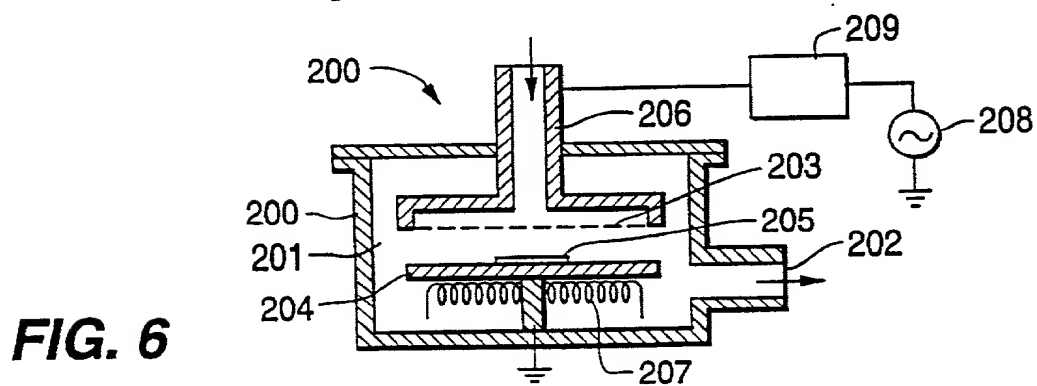
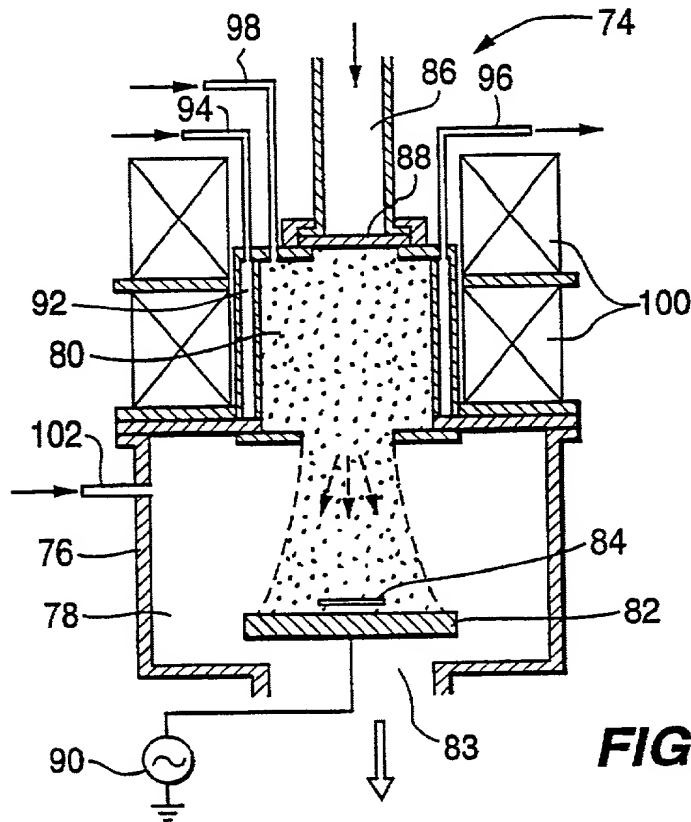
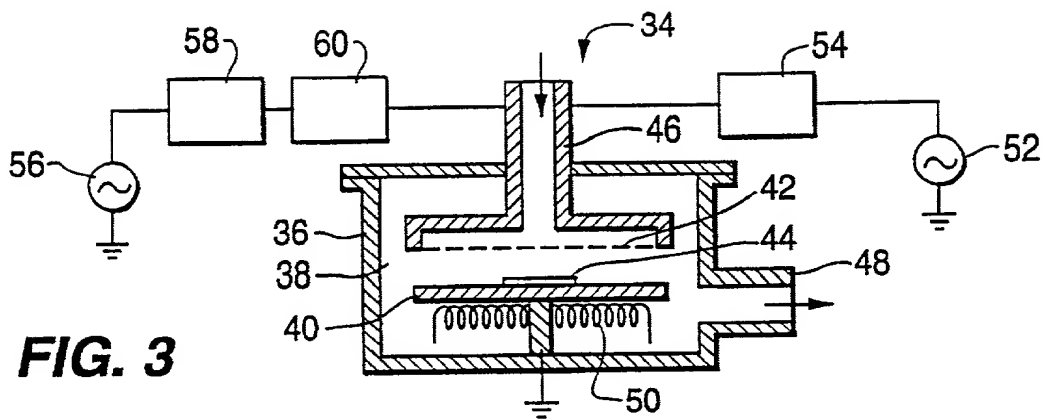


FIG. 2F
PRIOR ART



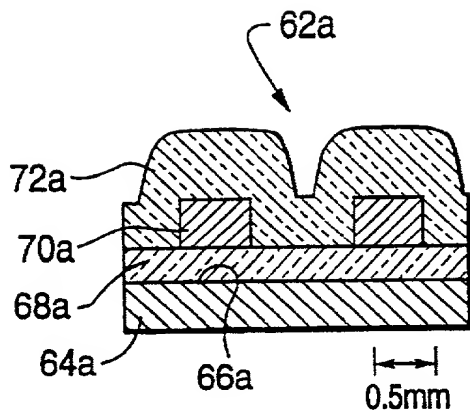


FIG. 4A

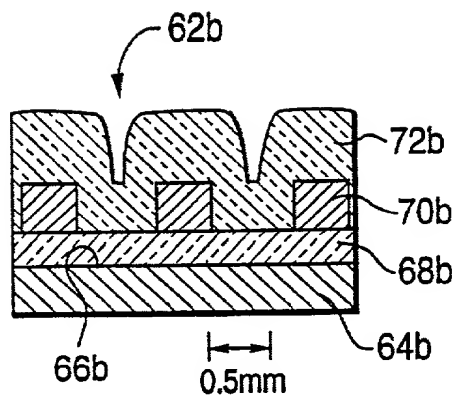


FIG. 4B

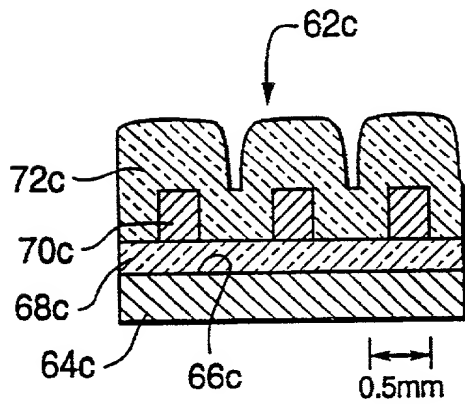


FIG. 4C

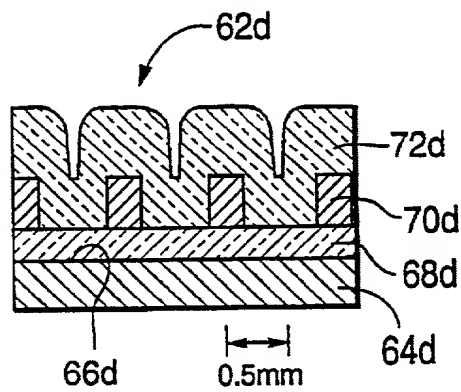


FIG. 4D

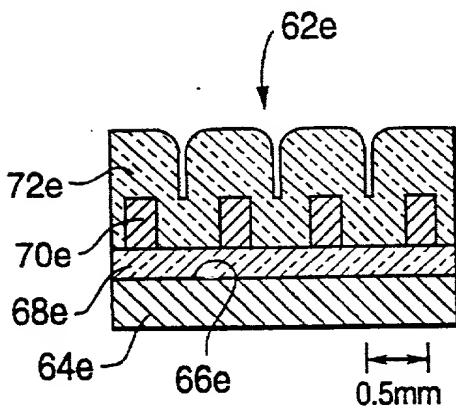


FIG. 4E

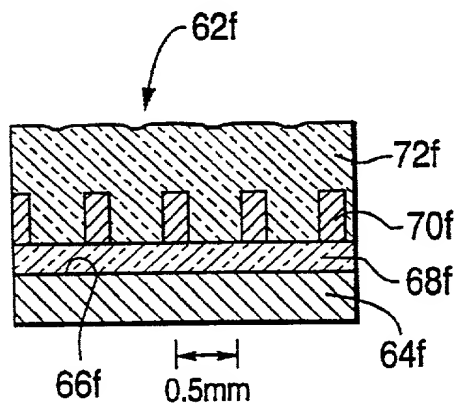


FIG. 4F

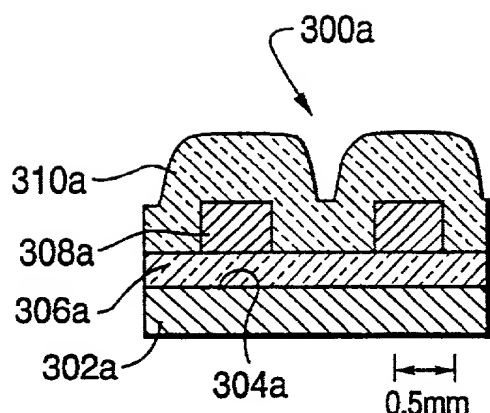


FIG. 7A

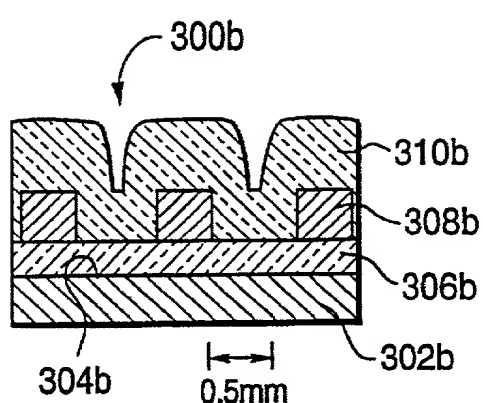


FIG. 7B

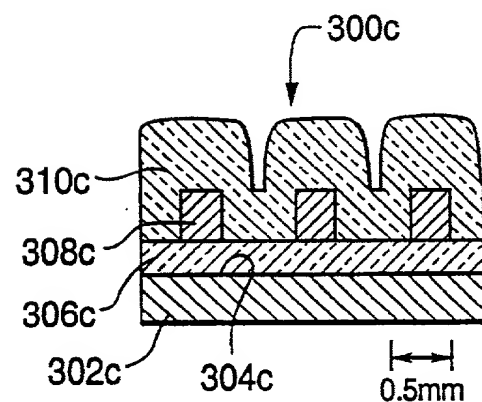


FIG. 7C

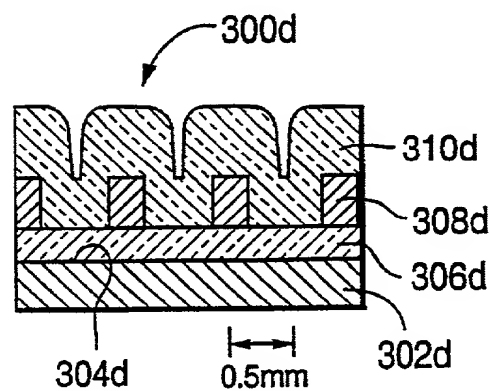


FIG. 7D

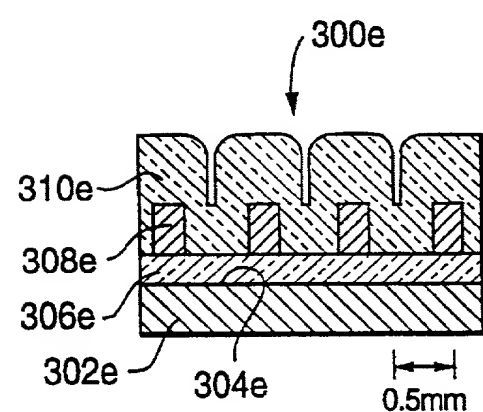


FIG. 7E

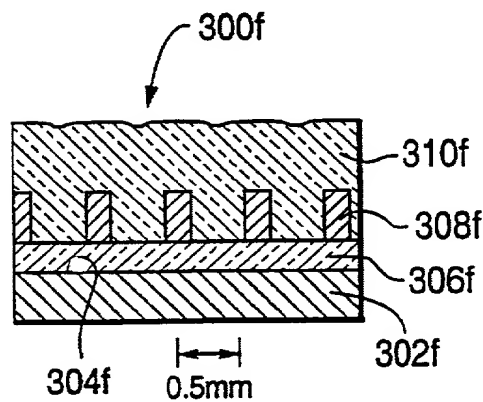
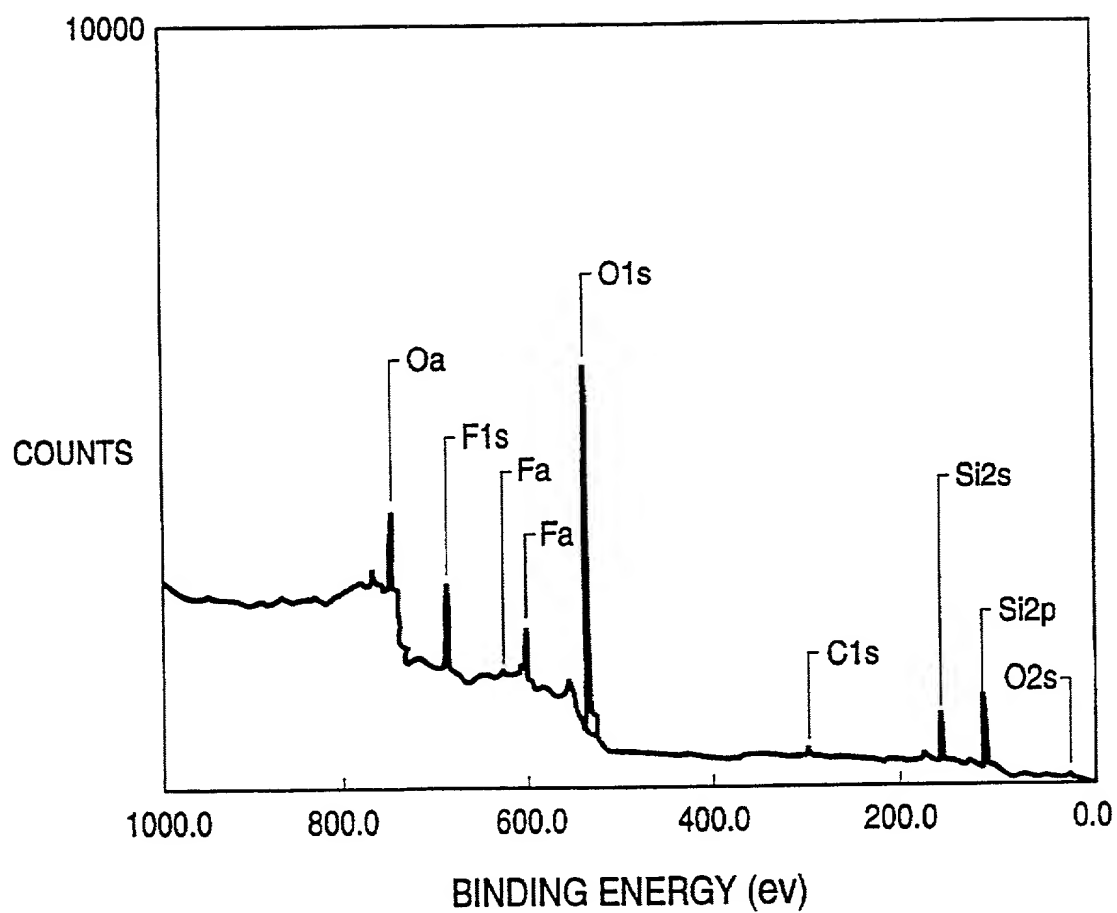


FIG. 7F



XPS SPECTRUM FOR C₂F₆ DOPED PE-TEOS FILM.

FIG. 8A

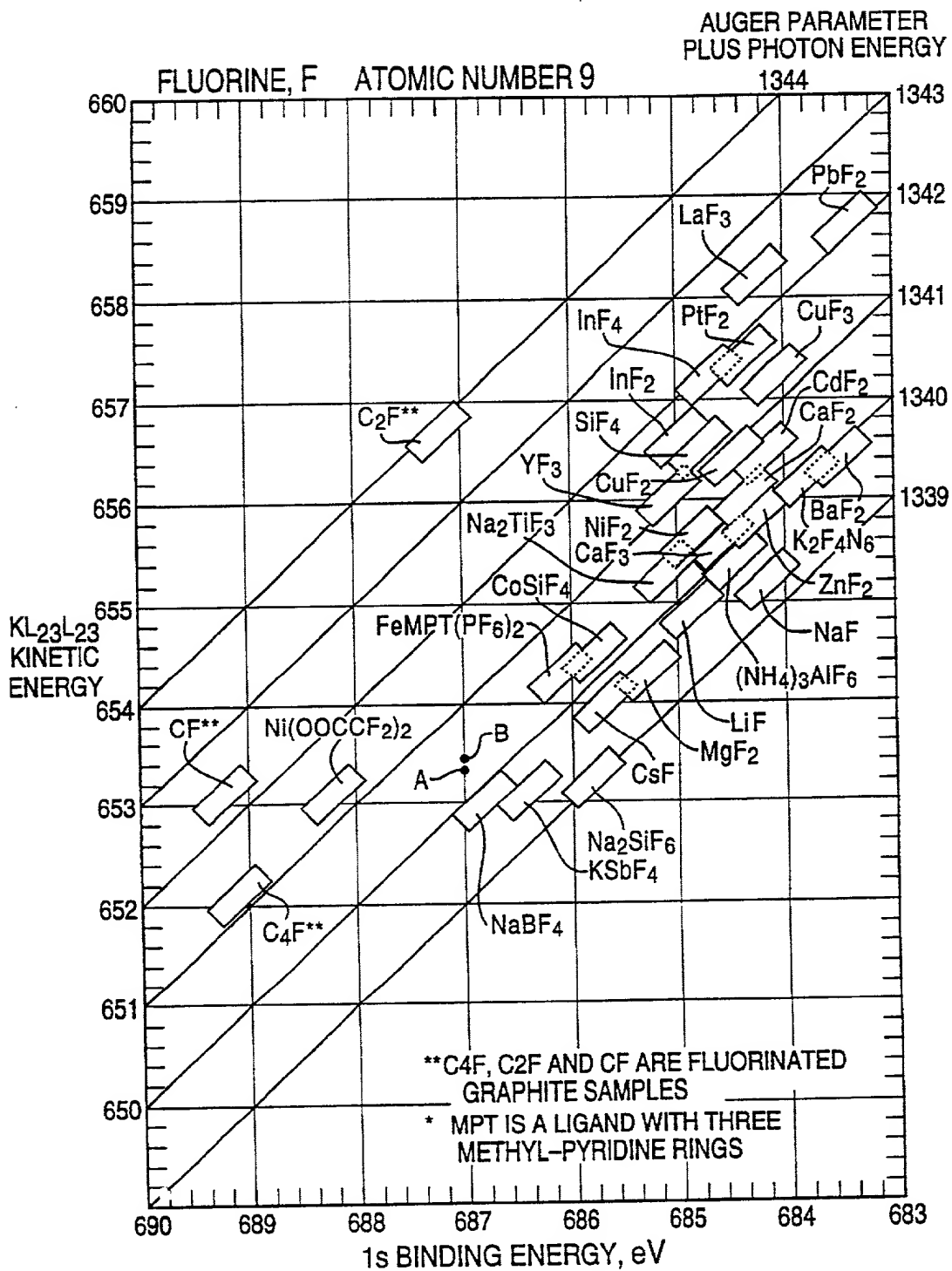


FIG. 8B

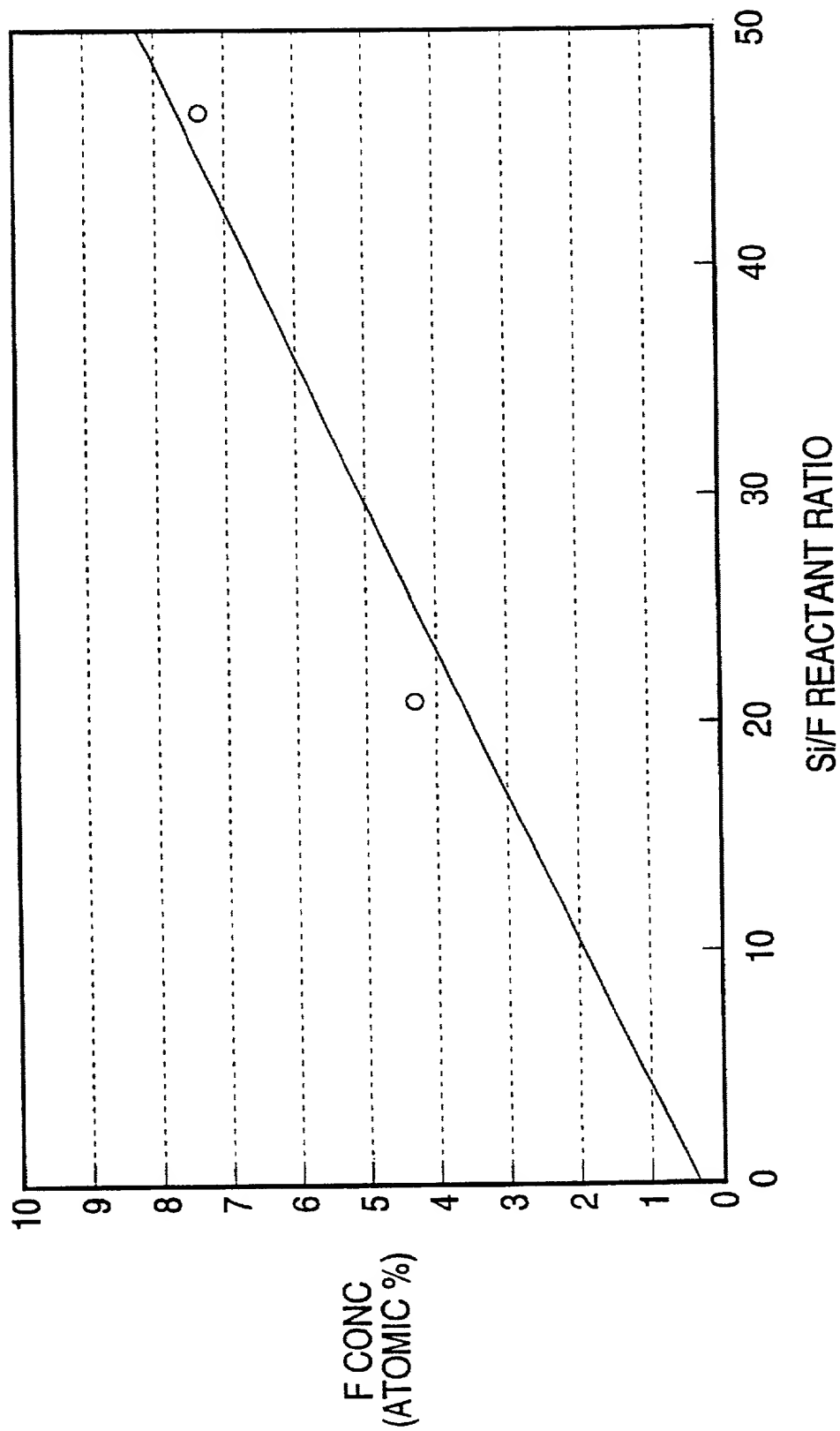


FIG. 9

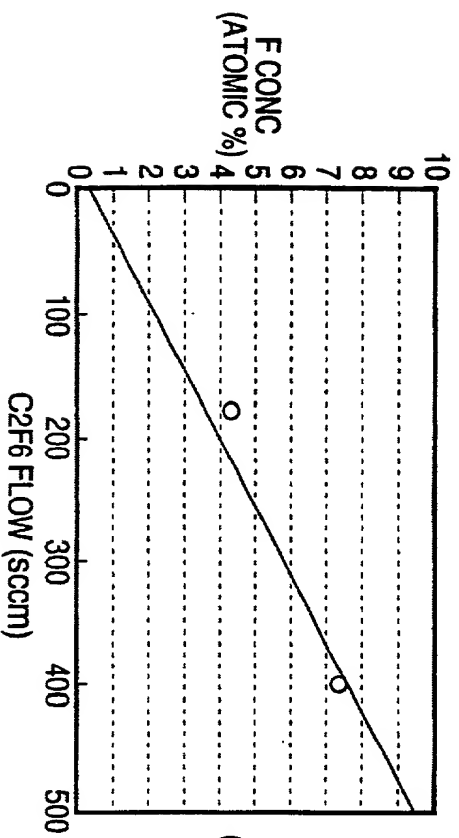


FIG. 10

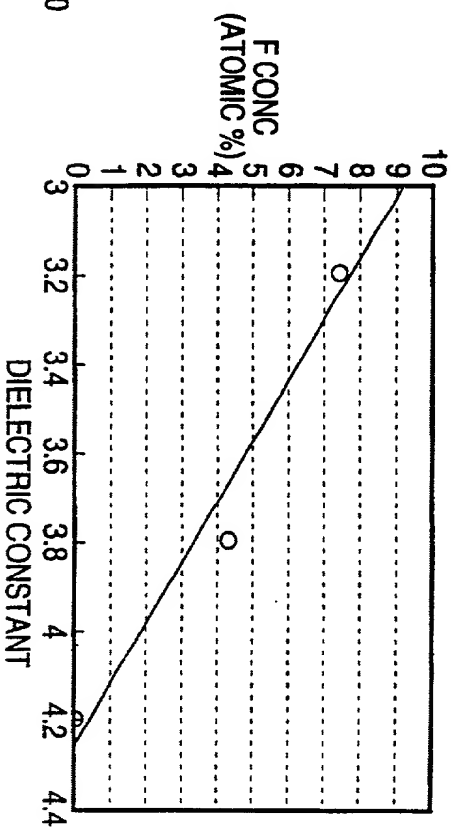


FIG. 11

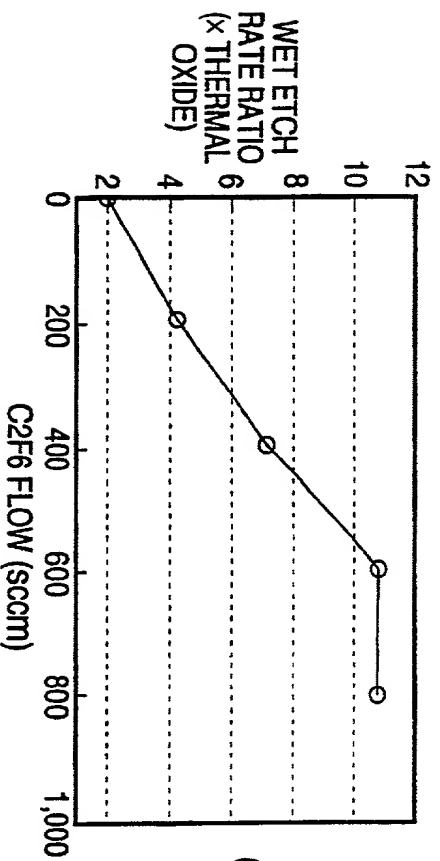


FIG. 12

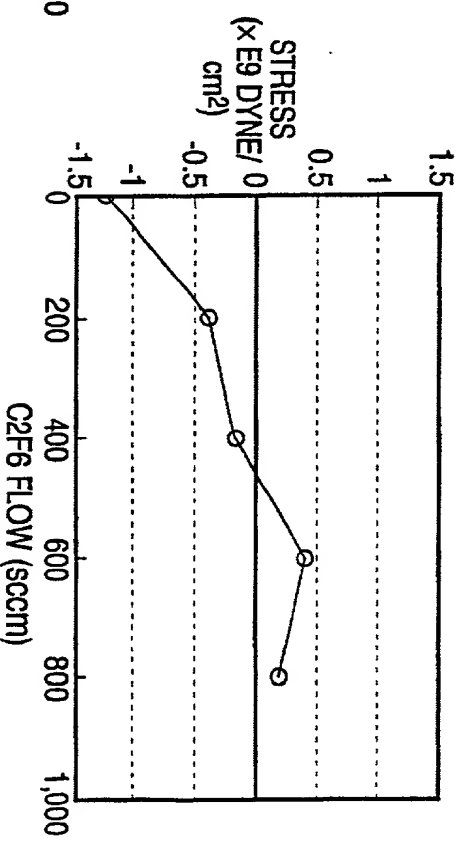


FIG. 13

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NO. 6076 P. 10/12

Attorney Docket No.: AMAT 524R1/T289

DECLARATION

As a below named inventor, I declare that:

My residence, post office address and citizenship are as stated below next to my name; I believe I am an original, first, and joint inventor of the subject matter which is described in U.S. Patent No. 5,571,571, issued November 5, 1996, and for which a broadening reissue patent is sought on the invention entitled METHOD FOR FORMING A THIN FILM FOR A SEMICONDUCTOR DEVICE the specification of which is attached hereto.

I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, Section 1.56. I verily believe the original patent to be wholly or partly inoperative or invalid by reason of the patentees claiming less than they had the right to claim in the patent. One error upon which the reissue is based is that the patent does not claim a method of depositing a layer having a predetermined stress level by distributing a halogen source at a selected rate to a processing chamber.

All errors corrected in this reissue application arose without any deceptive intention on the part of the applicant.

PRIORITY CLAIM (35 U.S.C. §119)

I hereby claim foreign priority benefits under Title 35, United States Code, §119, of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below, and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed.

Prior Foreign Application(s)

| Country | Application No. | Date of Filing | Priority Claimed Under 35 USC 119 |
|---------|-----------------|----------------|---|
| Japan | 5-145070 | June 16, 1993 | Yes <input checked="" type="checkbox"/> No <input type="checkbox"/> |

PRIORITY CLAIM (35 U.S.C. §120)

I claim the benefit under Title 35, United States Code, Section 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, section 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, section 1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

| Application No | Date of Filing | Status |
|----------------|------------------|--|
| 08/184,331 | January 19, 1994 | Patented Pending <input checked="" type="checkbox"/> Abandoned |

| Full Name of Inventor 1: | Last Name: | First Name: | Middle Name or Initial: |
|--------------------------|---------------------------|-----------------------|-------------------------|
| Residence & Citizenship: | MUSAKA | KATSUYUKI | |
| Post Office Address: | City | State/Foreign Country | Country of Citizenship |
| | Izumi | Chiba 270-1505 | Japan |
| | Post Office Address | City | State/Country |
| | 4-3-6 Ryukakujidai, Sakae | Izumi, Chiba 270-1505 | Japan |
| | | | Postal Code: |


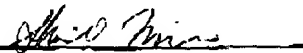
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NO. 6076 P. 11/12

Attorney Docket No.: AMAT 524R1/T289

| | | | |
|--------------------------|---|---|---------------------------------|
| Full Name of Inventor 2: | Last Name: MIZUNO | First Name: SHINSUKE | Middle Name or Initial: |
| Residence & Citizenship: | City Inba | State/Foreign Country Chiba 270-1505 | Country of Citizenship Japan |
| Post Office Address: | Post Office Address 3-9-11 Ryukakujidai, Sakae | City Inba, Chiba 270-1505 | State/Country Japan |

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

| | |
|--|--|
| Signature of Inventor 1  KATSUYUKI MUSAKA | Signature of Inventor 2  SHINSUKE MIZUNO |
| Date 11/5/98 | Date November 5, 1998 |

RECEIVED 11/5/98